COMMUNICATIONS RECEIVED SINCE THE END OF THE SESSION.

I. "On a New Class of Bodies Homologous to Hydrocyanic Acid."—I. By A. W. HOFMANN, LL.D., F.R.S. Received August 20, 1867.

The typical transformation which hydrocyanic acid undergoes when submitted, under appropriate circumstances, to the action of water, is capable of assuming two different forms when accomplished in its homologues.

If the hydrocyanic molecule be found to fix the elements of two molecules of water, yielding ultimately formic acid and ammonia, it is obvious that the atom group which in the homologues of hydrocyanic acid we assume in the place of hydrogen may be eliminated when these homologues are decomposed by water in conjunction either with formic acid or with ammonia. To take an example:—When acting with water upon the simplest homologue of hydrocyanic acid (upon cyanide of methyl), we may expect to see the methyl-group separating either in the form of methyl-formic, *i. e.* acetic acid, or in the form of methyl-ammonia, *i. e.* of methylamine. The difference of the two reactions and their relation to the metamorphosis of hydrocyanic acid itself are exhibited by the following equations:—

$$\underbrace{CHN}_{\text{Prussic acid.}} + 2H_2O = \underbrace{CH_2O_2}_{\text{Formic acid.}} + H_3N.$$

$$1.\ \underbrace{C_2H_3N}_{\text{Cyanide of methyl } \alpha.} + 2H_2O = \underbrace{C_2H_4O_2}_{\text{Methylformic (acetic) acid.}} + H_3N.$$

$$2.\ \underbrace{C_2H_3N}_{\text{Cyanide of methyl } \beta.} + 2H_2O = \underbrace{CH_2O_2}_{\text{Formic acid.}} + \underbrace{CH_5N.}_{\text{Methylamine.}}$$

The former one of these processes of transformation is familiar to chemists from the study of the hydrocyanic ethers or nitriles. The first member of this remarkable group of bodies (cyanide of ethyl) was discovered by Pelouze; the general character of their transformation was subsequently established by the beautiful investigations of Kolbe and Frankland on the one hand, and by those of Dumas, Malaguti, and Le Blanc on the other.

Researches in which I have been engaged during the last few weeks have proved that the second process of transformation does not less frequently occur. Indeed I have found that there corresponds to each of the hydrocyanic ethers or nitriles known hitherto, a second body of precisely the same composition but of absolutely different properties. These substances, when changed by water, undergo the transformation which is exhibited by the last one of the three above equations.

A happy experiment has led me to the discovery of this new class of bodies. In a lecture I wanted to exhibit the interesting transformation of

ammonia into prussic acid by means of chloroform, which was first observed by M. Cloez, and which illustrates so well our present views on quantivalence. When the two substances alone are allowed to act upon one another, this reaction can be rapidly accomplished only at a high temperature and consequently under pressure. In order to shorten the process (in one word, in order to exhibit this important reaction in a lecture-experiment), I had added potash to the mixture for the purpose of fixing the newly formed prussic acid, and was delighted to find that a few seconds' ebullition was sufficient to yield a considerable amount of cyanide of potassium, so as to furnish, after the addition of the two salts of iron, a large quantity of Prussian blue. On subsequently repeating the experiment with some of the derivatives of ammonia, more especially with several primary monamines, I was astonished to observe in each case a powerful reaction giving rise to the evolution of vapours of an almost overwhelming odour, strongly recalling that of prussic acid. But few experiments were necessary for the purpose of isolating the odoriferous bodies. The compounds thus formed are the substances isomeric with the hydrocyanic ethers or nitriles hitherto examined.

From the host of bodies which were thus suddenly thrown into view, it was necessary to single out the compound of a particular series in order to determine by accurate experiments the nature of the new reaction. The facility of procuring the necessary material, as well as old predilections, suggested the phenyl-series as the one to be examined in the first place. I beg leave to submit to the Royal Society a brief account of the mode of preparation, and of the principal properties, of the new derivative of aniline.

Cyanide of Phenyl.

A mixture of aniline, chloroform, and alcoholic potash yields on distillation a liquid of a powerfully aromatic but, at the same time, hydrocyanic-acid-like odour. The vapour of the liquid gives rise to a peculiar bitter taste, and causes, moreover, in the throat the suffocating sensation so characteristic of hydrocyanic acid. On redistilling the liquid, alcohol and water pass first, and ultimately an oily body is procured, which, in addition to the smelling substance, still contains a large amount of aniline. The latter is separated by oxalic acid, when the powerfully smelling compound remains in the form of a brownish oil. Freed from water by hydrate of potassium and purified by distillation, the new body presents itself as a mobile liquid, exhibiting a greenish colour in transmitted, and a beautifully blue colour in reflected light. This colour does not disappear by distillation even in a current of hydrogen.

The analysis of the blue oil has established the formula

$$C_7 H_5 N.$$

The compound is thus seen to be isomeric with benzonitrile, discovered by Fehling, from which it differs, however, in all its properties. In order to distinguish the new compound from benzonitrile I will call it *cyanide of*

phenyl, without intending, however, by selecting this name, to express any particular view as to its constitution. The formation of cyanide of phenyl is represented by the following equation:—

$$\underbrace{C_6H_7N}_{\text{Aniline.}} + \underbrace{CHCl_3}_{\text{Chloroform.}} = \underbrace{C_7H_5N}_{\text{Cyanide of phenyl.}} + 3HCl.$$

Cyanide of phenyl cannot be volatilized without undergoing decomposition. During distillation the thermometer marks for some time the constant temperature of 167°, which may be taken as the boiling-point of cyanide of phenyl. Then the temperature rises rapidly to from 220° to 230°. The brown liquid which now distils is destitute of odour, and solidifies on cooling to a crystalline mass, easily purified by solution in alcohol, but not yet more minutely examined. Cyanide of phenyl is remarkable for the facility with which it combines with other cyanides. The compound with cyanide of silver is particularly beautiful. The behaviour of cyanide of phenyl with acids is more especially characteristic. Scarcely changed by the action of alkalies, it cannot be left in contact even with moderately dilute acids without undergoing alteration. When submitted to the action of concentrated acids, the liquid bursts into ebullition, and the solution, after cooling, contains only formic acid and aniline.

$$\underbrace{C_7H_5N}_{\text{Cyanide of phenyl.}} + 2H_2O = \underbrace{CH_2O_2}_{\text{Formic acid.}} + \underbrace{C_6H_7N}_{\text{Aniline.}}$$

Benzonitrile, isomeric with cyanide of phenyl, is known to be slowly attacked by acids, but to be rapidly transformed by alkalies into benzoic acid and ammonia.

$$\underbrace{C_7H_5N}_{\text{Benzonitrile.}} + 2H_2O = \underbrace{C_7H_6O_2}_{\text{Benzoic acid.}} + H_3N.$$

The transformation of benzonitrile into benzoate of ammonium, as, indeed, the transformation of the nitriles into the ammonium-salts of the respective acids generally, is not accomplished in one single bound. By fixing only one molecule of water, benzonitrile is first converted into benzamide,

$$\underbrace{C_7H_5N}_{\text{Benzonitrile.}} + H_2O = \underbrace{C_7H_7NO}_{\text{Benzamide.}}$$

Nor is the corresponding term of the isomeric series wanting. This substance has long been known as phenyl-formamide or formanilide,

$$\underbrace{C_7H_5N}_{\text{Cyanide of phenyl.}} + H_2O = \underbrace{C_7H_7NO}_{\text{Phenyl-formamide.}}$$

But, in addition to phenyl-formamide, there figures in this series a second intermediate compound, the analogue of which among the derivatives of

benzonitrile is not yet perfectly known*. This compound is the well-defined base which some time ago I described as methenyldiphenyldiamine, and which may be looked upon as formed by the association of a molecule of cyanide of phenyl with a molecule of aniline. The successive changes which cyanide of phenyl undergoes when submitted to the influence of water are thus exhibited by the following series of equations :—

$$\underbrace{C_{14}H_{10}N_2}_{\text{2 mols. cyanide of phenyl.}} + 2H_2O = \underbrace{CH_2O_2}_{\text{Formic acid.}} + \underbrace{C_{13}H_{12}N_2}_{\text{Methenyldiphenyldiamine.}}$$

$$\underbrace{C_{13}H_{12}N_2}_{\text{Methenyldiphenyldiamine.}} + H_2O = \underbrace{C_7H_7NO}_{\text{Phenylformamide.}} + \underbrace{C_6H_7N}_{\text{Aniline.}}$$

$$\underbrace{C_7H_7NO}_{\text{Phenylformamide.}} + H_2O = \underbrace{CH_2O_2}_{\text{Formic acid.}} + \underbrace{C_6H_7N}_{\text{Aniline.}}$$

A glance at these formulæ shows that the metamorphosis of phenylic cyanide is perfectly analogous to that of phenylic cyanate, which I have studied at an earlier date.

$$\underbrace{C_{14}H_{10}N_2O_2}_{\text{2 mols. cyanate of phenyl.}} + 2H_2O = \underbrace{CH_2O_3}_{\text{Carbonic hydrate.}} + \underbrace{C_{13}H_{12}N_2O}_{\text{Diphenyl-urea.}}$$

$$\underbrace{C_{13}H_{12}N_2O}_{\text{Diphenyl-urea.}} + H_2O = \underbrace{C_7H_7NO_2}_{\text{Anhydrous carbonate of aniline.}} + \underbrace{C_6H_7N}_{\text{Aniline.}}$$

$$\underbrace{C_7H_7NO_2}_{\text{Anhydrous carbonate of aniline.}} + H_2O = \underbrace{CH_2O_3}_{\text{Carbonic hydrate.}} + \underbrace{C_6H_7N}_{\text{Aniline.}}$$

In conclusion, I may state that I have submitted ethylamine, amylamine, and toluidine to the action of chloroform. The phenomena are, as might have been expected, perfectly analogous. Indeed the application of the new reaction to the different classes of the ammonia derivatives, to the amides, to the diamines and triamines, and perhaps even to some of the natural alkaloids, promises a rich harvest of results. Should I have the good fortune of gathering some of these, I shall not fail to present them to the Society, which has so generously encouraged and assisted my earlier researches in the field of organic chemistry.

* Shortly before his death, Gerhardt was engaged in experiments on the action of pentachloride of phosphorus on the amides, a brief account of which was subsequently published by M. Cahours. Among other substances, I find that, by acting with pentachloride of phosphorus upon benzanilide, Gerhardt obtained a chloride, $C_{13}H_{10}NCl$, which yields with ammonia a crystalline substance. It can scarcely be doubted that this compound is the derivative of benzonitrile corresponding to methenyldiphenyldiamine,

$$C_{13}H_{10}NCl + H_3N = C_{13}H_{12}N_2 + HCl.$$